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Method For Preparing Self-assembled Silicon Nanotubes By

Hydrothermal Method

FIELD OF THE INVENTION

The present invention is related to the method for the preparation of self-assembled silicon nanotubes (SiNTs), in particular, to the method for the synthesis of self-assembled SiNTs from inorganic solution (hydrothermal solution).

BACKGROUND TECHNOLOGY

Although the difficulty for the synthesis of SiNTs is widely attributed to the sp^3 hybridization in silicon, the possibility of the existence of SiNTs has been suggested theoretically. The preparation of SiNTs, especially self-assembled SiNTs is still very challenging at present. Great interest has focused on carbon nanotubes (CNTs) owing to its excellent properties, which is hot topic worldwide. Many researchers are attempting to prepare self-assembled SiNTs. Recently SiNTs were prepared using template method respectively by Jeong and his coworkers in Sungkyunkwan University, and Sha and his coworkers in Zhejiang University. The corresponding research results were published in Advanced Materials (Adv Mater) which is a famous international journal in the field of materials. SiNTs with the outer diameter of less than 100nm were synthesized by Jeong and his coworkers using alumina templates. The templates were brought into the molecular beam epitaxy (MBE) chamber where the chamber was evacuated to a pressure of 5×10^{-10} Torr. The Si atoms/clusters were sputtered for 10min by electron-beam evaporator. The temperature of alumina

templates was maintained at 400°C. After the deposition, the sample was further heat treated at 600°C or 750°C under ambient conditions for oxidation. SiNTs with the outer diameter of less than 100nm were also fabricated by Sha and his coworkers using a nanochannel Al₂O₃ (NCA), silane as the silicon source, gold as the catalyst in the case of 620°C、1450Pa by chemical vapor deposition (CVD) process. Although SiNTs had been prepared by the alumina template and NCA, the SiNTs were formed in the inner wall of templates, not independent on the self-assembled growth of element Si. Therefore SiNTs obtained by the templates are not the real SiNTs.

DESCRIPTION OF THE INVENTION

The purpose of the invention is to prepare self-assembled SiNTs with silicon source materials, but without metallic catalysts and templates. The method takes great advantages of simple process, easy to operate and control the equipment, low cost and without the pollution, and is a kind of hydrothermal method to prepare self-assembled SiNTs with small diameter and uniform diameter distribution.

The preparation of self-assembled SiNTs can be performed by the following process: Water is the solvent. The rate of silicon oxide and water is from 0.01 to 10wt%. The silicon oxide and water are mixed, and then the mixture is put into sealed reaction kettle under the condition of 200~500°C, 3~40MPa and is maintained for 1-5h with the equably stirring.

The mixture is stirred using the magnetic stirrer.

In preferably, the rate of silicon oxide and solvent is 0.05-8wt%.

In further preferably, the rate of silicon oxide and solvent is 0.1-6wt%.

The self-assembled SiNTs can be prepared under the preferred conditions of 250-500°C of temperature, 8-35MPa of pressure and the temperature and pressure will be maintained for 1-4h with the equably stirring.

The more preferred preparation conditions in present invention are as follows:

Temperature: 300-450°C. Pressure: 10-30MPa. The temperature and pressure will be maintained for 1-3h with the equably stirring.

The other more preferred preparation conditions in present invention are as follows:

Temperature: 300-400°C. Pressure: 6-10MPa. The temperature and pressure will be maintained for 3-4h with the equably stirring.

No metallic catalysts and templates are used in the preparation method disclosed in present invention. The SiNTs prepared by present invention are identified as a kind of self-assembled SiNTs according to the results of characterization. The shortages of the common nanoscale materials reuniting easily and dispersing difficultly in the prior art are overcome because the self-assembled SiNTs are obtained from the water solution in which no reuniting and intertwist happen. At the same time, the self-assembled SiNTs makes it possible to increase the strength and toughness of composite, owing to the SiNTs with large rate of length and diameter. A great deal of research shows that silicon nanowire (SiNWs) have greatly potential and practical applications owing to its typical quantum confinement effect and excellent physical properties. However, theoretical research shows that SiNTs can take advantage of the quantum confinement effect more easily and more stably than SiNWs. Therefore, SiNTs are predicted to have the promising for the application in nanodevices in the future and become a new

nanoscale material in nanotechnology field, which provides a new approach for the nanodevices to be highly integrated and miniaturized. The preparation of present invention is simple, operating easily, and simple equipment is used and the cost is low. This preparation creates the opportunity for the practical applications of the self-assembled SiNTs. Innocuous starting materials are used in the invention. The starting materials and preparation process are all unpolluted to the environment absolutely, which accords with the development trend of modern industry for environment protection. Therefore, the large quantities of self-assembled SiNTs can be prepared industrially.

The growth mechanism of the self-assembled SiNTs prepared by present invention is simply introduced as the following: Self-assembled growth mechanism of SiNTs is proposed preliminarily according to the “lip-lip” interaction growth model proposed by Charlier et al. During the growth phase of the nanotubes, chemical bondings at the end of nanotubes (NTs) in a metastable energy minimum, prevents the closure of the growth end of NTs. The atoms of forming nanotubes connect with each other continuously resulting in the sustaining growth of NTs. With the change of conditions, such as the decrease of temperature, the chemical bonding of the growth end of NTs is tending to stable state resulting in the closure of the growth end of NTs because the closed structure is more stable than the initial open end structure. Fig. 1 is the growth process schematic of self-assembled SiNTs. Chemical bondings between atoms are all in metastable state and abundant H^+ , Si atoms and O^{2-} atom occur because Si and silicon oxide are in the state of gaseity and react between them also occurs under

high temperature and high pressure of hydrothermal condition. Nucleation starts relatively equably from the vapor substances in the reaction kettle owing to the equably stirring of magnetic stirrer in the preparation process. Then temperature rising rapidly in the kettle shows that much heat is given out demonstrating the growth process of the SiNTs. There is a temperature field, i.e. temperature grads from high temperature area in the center to low temperature area in the edge of reaction kettle. The tubular structures are elementarily formed in the low temperature area due to combining Si and Si during the growth of SiNTs (Fig. 1(a)). Si-Si bonding in the growth edge of the tubular structures in a metastable energy minimum prevents the closure of growth edge of SiNTs. At the same time, collision opportunity increases because SiNTs move continually between low temperature area and high temperature area with the stirring of stirrer. Thus abundant Si atoms in high temperature area enter into the tubular walls of SiNTs and are combined with Si of tubular wall resulting in the one-dimensional growth of SiNTs along the temperature field direction. The stable SiO₂ layers form by the reaction of Si atoms in the interface of tube and atoms O²⁻ in the environment preventing the growth of SiNTs in non-one-dimensional direction (Fig. 1(b)). Because abundant H⁺ exists in the hydrothermal condition, thus one of four Si atoms in the crystalline Si is substituted by H⁺ and a part of crystalline Si in the tubular wall of SiNTs is possible to become amorphous Si resulting in the formation of crystalline Si layers with similar graphite layer structure. Si-Si bondings in the growth end of SiNTs is changing from the metastable state to the stable state gradually due to the falling of temperature and pressure after heating is stopped.

Simultaneously the temperature grads in the kettle also disappear gradually resulting in the closure of the growth end and the growth of SiNTs stops (Fig. 1(c), (d)).

BRIEF DESCRIPTIONS OF THE DRAWINGS

Fig. 1 is the self-assembled growth schematic of the self-assembled SiNTs.

Fig. 2 is the transmission electron microscopy (TEM) image of the self-assembled SiNTs prepared in the invention.

Fig. 3 is the selected area electron diffraction (SAED) image of the self-assembled SiNTs prepared in the invention.

Fig. 4 is the energy dispersive X-ray spectroscopy (EDS) of the self-assembled SiNTs prepared in the invention.

Fig. 5 is the high-resolution transmission electron microscopy (HRTEM) image of tubular body of the self-assembled SiNTs prepared in the invention.

Fig. 6 is the HRTEM image of tubular growth tip of the self-assembled SiNTs prepared in the invention.

The TEM image of the self-assembled SiNTs in Fig. 2 shows that abundant of nanotubes are visible in the figure. Most nanotubes are in straight shape and the surface of self-assembled SiNTs is smooth. The outer diameter is common less than 5nm, the distribution range is 8~20nm, and the length of SiNTs is several hundreds of nanometers, up to microns. The diameter of inner pore is smaller than 5nm in general with a small diameter distribution range. The growth tips of the self-assembled SiNTs are in closed semicircular form showing that no catalyst particles exist in the SiNTs

and no growth tips with open end structure are observed.

The SiNTs is a kind of poly-crystalline structure according to the SAED pattern (Fig. 3) of the self-assembled SiNTs. In that pattern, the first, second, third order diffraction rings respectively match well with the (1 1 1), (2 2 0) and (3 1 1) diffraction crystal plane.

EDS analysis in Fig. 4 shows that the chemical composition of the products only consists of Si and O and the peak height of Si and O is same. The atomic ratio of Si and O is 1:1 which accords with that of silicon monoxide.

The interplanar spacing, outer diameter and the diameter of inner pore, the thickness of amorphous outer layer and Si wall layer of the SiNTs were measured according to the HRTEM measurement and following calculation by the software of Digital Micrograph applied in the HRTEM. The hollow inner pore, crystalline silicon wall layer and amorphous silica outer layer can be observed obviously from the HRTEM images. The crystalline grows along the axial direction of SiNTs. The interplanar spacing of crystalline in the SiNTs is around 0.31nm according to the measurement and calculation matching well with the {111} plane of silicon. The outer diameter of the tubular body in Fig. 5 is about 14nm, the diameter of inner pore is about 5nm and the thickness of crystalline Si and amorphous outer layer are about 5nm and less than 2nm respectively. The outer diameter of the tubular growth tip in Fig. 6 is about 18nm and the diameter of inner pore is about 3nm which is larger than that of the tubular body. The corresponding thickness of Si wall is 5nm and amorphous outer layer less than 2nm. The amorphous silicon oxide outer layer in the

growth tip of the self-assembled SiNTs distributes asymmetrically and some defects exist in the SiNTs. The amorphous outer layers can be identified to be amorphous silica oxide because the environment in the reaction kettle is a kind of oxidation environment, only silicon and oxygen exist in the sample and silica oxide is the most stable compound of silica. The appearance of the same number of lattice fringes and amorphous silica outer layers from both sides of the self-assembled SiNTs shows that it has a seamless tubular structure. Therefore, the structures of SiNTs are composed of three parts: hollow inner pore with a diameter of several nanometers in the middle, crystalline silicon wall layer with a thickness of less than 5nm and amorphous silica outer layers with less than 2nm.

EMBODYMENTS

1. Silicon oxide and water with a rate of 0.01wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 200°C of temperature, 3MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer.

2. Silicon oxide and water with a rate of 0.1wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 380°C of temperature, 8MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer.

3. Silicon oxide and water with a rate of 0.5wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 500°C of temperature, 8MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer.

4. Silicon oxide and water with a rate of 1wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 300°C of temperature, 10MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer.

5. Silicon oxide and water with a rate of 4wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 380°C of temperature, 15MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer.

6. Silicon oxide and water with a rate of 6wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 500°C of temperature, 20MPa of pressure and the temperature and pressure are maintained for 1h with the equably stirring of magnetic stirrer.

7. Silicon oxide and water with a rate of 6wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less

than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 380°C of temperature, 8MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer.

8. Silicon oxide and water with a rate of 8wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 500°C of temperature, 30MPa of pressure and the temperature and pressure are maintained for 2h with the equably stirring of magnetic stirrer.

9. Silicon oxide and water with a rate of 10wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 500°C of temperature, 30MPa of pressure and the temperature and pressure are maintained for 4h with the equably stirring of magnetic stirrer.

10. Silicon oxide and water with a rate of 8wt% were mixed and then put into sealed reaction kettle. Self-assembled SiNTs with the average diameter of inner pore of less than 5nm and around 15nm in the average outer diameter were prepared under the conditions of 450°C of temperature, 30MPa of pressure and the temperature and pressure are maintained for 3h with the equably stirring of magnetic stirrer.